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Hot Corrosion in Gas Turbines

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A review is presented which gives a brief, largely chronological overview of the development of the different theories of hot corrosion. This review was the Keynote Lecture for the Gas Turbine Session of the Symposium on Corrosion in Fossil Fuel Systems, Electrochemical Society Meeting, Detroit, MI, October 1982.

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HOT CORROSION IN GAS TURBINES[*]

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INTRODUCTION

Since the 1950's, a number of theories concerning the
mechanism of hot corrosion in gas turbines have been developed.
These theories have been discussed extensively at hot corrosion
and high temperature materials conferences and in various
reviews. However, many uncertaininties still exist as to how the
different theories relate to one another, and as to which, if
any, is 'correct'. Also there have been significant recent
developments, notably in 'low temperature' hot corrosion, which
have not been reviewed. This review provides a brief overview of
hot corrosion mechanism theory, with some historical perspective,
to illustrate how we have arrived at our current understanding of
hot corrosion.

Hot corrosion remains a serious problem for industrial and
marine gas turbines, especially as use of low quality petroleum
or alternate source fuels is contemplated. Although drastic
corrosion within a few hundred hours is now seldom seen, hot
corrosion is still the major life limiting factor in many
applications. In 1975, it was estimated that more than 50% of
the repair of electricity generating gas turbines was
necessitated by hot corrosion (1).

The literature cited in the present review is not
exhaustive, but only that necessary to trace the development of
the different theories. For more detailed study of hot
corrosion, the reader may be referred to several books (2-5)and
reviews (6-9). The proceedings of the DOE/EPRI Conferences on
Alternate Fuel Usage in Heat Engines (10,11), the UK/US Navy
Conferences on Marine Gas Turbine Materials (12,13), and the COST-

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50 Conferences on European Gas Turbine Material Development (14,15) are also important sources of information. Two earlier books on boiler fireside corrosion (16,17), which contain relevant sulfate and vanadate chemistry, may be recommended as well.

The different hot corrosion mechanism theories are largely determined by what one considers to be the corrodent. Table 1 lists the principal species identified as degrading gas turbine blades, along with the common description of the mode of attack (or mechanism) and the approximate operative temperature range. Carbon is not listed, although considerably studied and undoubtedly involved in hot corrosion under some circumstances, because its role seems to be principally through reduction of Na_2SO_4, or erosion by pyrolytic graphite particles. Similarly, vanadium is not listed separately since it is ordinarily not found as the predominant corrodent in gas turbines. Some believe, however, that V_2O_5 may lead to acidic fluxing in molten Na_2SO_4, and V_2O_5 effects are thus included under the 'acidic fluxing' heading in Table 1.

TABLE 1

Species Degrading Gas Turbine Blades

Corrodent	Mechanism	Temp. (C)
O_2	oxidation	>1000
Na_2SO_4	hot corrosion, sulfidation	850-950
SO_2	sulfidation-oxidation	650-950
Na_2O	basic fluxing	850-950
MoO_3 (WO_3, V_2O_5)	acidic fluxing	850-950
eutectic sulfates ($CoSO_4$-Na_2SO_4)	low temperature hot corrosion (LTHC)	650-750
NaCl	chloride attack	650-950

OXIDATION

Gas turbine blade metals and coatings react with oxygen to form protective surface oxides. Depending on the metal composition, these surface oxides will be predominantly Al_2O_3 or Cr_2O_3, with Cr_2O_3 being thought to provide more resistance to hot corrosion (e.g., ref. 18). Oxidation studies at 1000-1100°C of the ternary Ni-Cr-Al and Co-Cr-Al systems have defined the tentative Cr and Al

concentrations necessary to produce either Al_2O_3 or Cr_2O_3 surface scales (19). Generally Cr_2O_3 forms on alloys with 15 wgt-% or more Cr and less than 5% Al, while Al_2O_3 forms on alloys with over 5% Al and over 5% Cr (Cr increases the Al activity, promoting Al_2O_3 formation). However, the chromium levels required for Cr_2O_3 formation often involve undesired compromise. Chromium interferes, for example, with the $Ni_3(Al,Ti)$ gamma prime precipitation strengthening of Ni-based superalloys, so that high strength alloys may contain 10% or less Cr, and form only Al_2O_3 surface oxide.

The oxidation protection afforded by Cr_2O_3 is poorer than that of Al_2O_3 at high temperature because of volatilization of the Cr_2O_3. An analysis by Rapp (20) indicates that vaporization as CrO_3 (g) and $CrO_2(OH)$ (g) may cause Cr_2O_3 to lose effectiveness at temperatures as low as 1000°C in gas turbines. Therefore, in attempting to increase hot corrosion performance by employing chromium levels that produce Cr_2O_3 surface oxides, one may reduce high temperature oxidation resistance. In fact, high temperature hot corrosion resistance may be reduced as well, since burner rig development tests of, e.g., high chromium (>30%) CoCrAlY coatings generally show improved performance at 700°C, but decreased resistance at 900°C compared to CoCrAlY coatings of 20-22% chromium.

Oxidation of multielement superalloys is complex, and not adequately described by characterizing different alloys simply as 'Al_2O_3 or Cr_2O_3 formers'. During initial oxidation, oxides of all the reactive elements are formed in proportion to their concentration in the alloy. Oxides with fast intrinsic growth rates, e.g., NiO or CoO, will overgrow the slower developing Cr_2O_3 and Al_2O_3 nuclei; however, these nuclei subsequently grow laterally, and (if the Cr or Al concentration is high enough) form slow growing, oxidation rate controlling Al_2O_3 or Cr_2O_3 layers beneath the outer NiO or CoO oxides. The isolated monoxides may then react with the inner layer to form $NiCr_2O_4$ etc. mixed spinels.

The surface oxide on a metal is thus a dynamic system, with structures and compositions that change during the initial oxidation process, and presumably in 'repair' processes occurring after mechanical or chemical attack. The resultant oxides therefore can not be considered 'pure'. The scales on alumina formers are known, for example, to contain TiO_2, Cr_2O_3, spinel and other oxides (21). Furthermore, when a corrosive salt is present (hot corrosion), the surface oxide may be uniquely altered. The scales on Nimonic 105 and IN 738 LC have been reported to change from predominantly Cr and Ni oxide to Al and Ti oxide during 750°C burner rig tests; similarly, Cr_2O_3-rich oxides on $(Na,K)_2SO_4$ coated IN 939

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at 900°C were observed to become enriched in spinel and NiO with time (21). The question arises in extended tests, however, as to whether the outer oxide is the 'protective oxide' or simply an adherent corrosion product.

The oxide existing on the blade surface therefore clearly has a controlling effect in hot corrosion, with Cr_2O_3 perhaps to be preferred over Al_2O_3. The surface oxides are not monolithic, however, and their composition and morphology may be expected to change during oxidation, and especially during hot corrosion.

HOT CORROSION BY SODIUM SULFATE

Many early instances of gas turbine corrosion (e.g., as compiled by Stringer (7)) were associated with molten Na_2SO_4 deposits on the blades. The deposits often contained Ca-, Mg- or other sulfates, but it was expected from phase diagrams that the molten phase would be Na_2SO_4-rich, and essentially represented by Na_2SO_4. Hot corrosion thus came to be defined as 'the corrosion caused by deposition of molten Na_2SO_4 on turbine blade surfaces'.

The Na_2SO_4 results from reaction of sulfur in the fuel (up to 0.40 wgt-% in JP-5; up to 2+ wgt-% in lower quality oil) with sodium impurities in the fuel or air influx. For the marine environment, the reaction is usually written as

$$2 \ NaCl + SO_3 + 1/2 \ O_2 = Na_2SO_4 + Cl_2 \qquad [1]$$

to indicate reaction between NaCl from sea salt and SO_3 produced by oxidation of fuel sulfur during combustion. Whether reaction [1] occurs within the combustor, in the transition zone, or on the blade surfaces, and whether vaporous or particulate NaCl is involved, remains a controversy (see Chloride Attack). A widely discussed theory by DeCresente and Bornstein (22) suggests that Na_2SO_4 occurs as a condensable vapor above the turbine blades (i.e., that reaction [1] is completed in the combustor or shortly after). Corrosion should be found therefore only for blade temperatures and Na_2SO_4 partial pressures below the 'dew point'; that is, conditions where Na_2SO_4 condenses on the blade. An analysis of corrosion in one engine has shown reasonable agreement with this theory (23), but the evidence overall does not seem sufficient to exclude other theories of Na_2SO_4 formation on blades.

Molten Na_2SO_4 (mp 884°C) induced hot corrosion of Ni-based superalloys is generally characterized by i) chromium sulfide formation in the metal, ii) an inner

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corrosion region consisting of oxides (mainly Cr_2O_3) and
Ni-rich metal fragments, and iii) an outer oxide layer
mostly of NiO. This has come to be known as the so-called
'high temperature hot corrosion' morphology.

One of the first reported in-depth investigations of
hot corrosion was by Simons et al (24) to explain
corrosion found in 1952 in a gas turbine burning Bunker C
fuel. They concluded that molten Na_2SO_4 per se had little
corrosive effect, and that reduced forms of sulfur,
produced by reaction with carbon or other reducing agents,
were the actual cause of hot corrosion. Two types of
attack were identified: 'catastrophic' occurring under
crucible test conditions (massive Na_2SO_4, low oxygen), and
'enhanced oxidation' occurring with thin film deposits
(limited Na_2SO_4, high oxygen). For catastrophic attack,
the suggested mechanism was

$$Na_2SO_4 + 3 R = Na_2O + 3 RO + S \qquad [2]$$

$$M + S = MS \qquad [3]$$

$$Na_2SO_4 + 3MS = 4 S + 3MO + Na_2O \qquad [4]$$
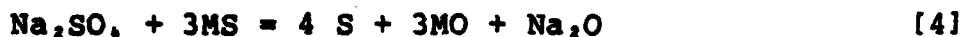
where R = reducing agent, and S = lower valence sulfur.
Reaction [2] was considering a triggering phase (sporadic
and unpredictable) which led to autocatalytic metal
destruction by reactions [3] and [4]. A continuous source
of Na_2SO_4 is required for this mechanism. The enhanced
oxidation mechanism was proposed to be

$$M + MS = M-MS \text{ (eutectic)} \qquad [5]$$

$$M-MS + 1/2 \ O_2 = MO + MS \qquad [6]$$

where MS forms initially by reactions [2] and [3]. Note
that the metal sulfide is not consumed, since it is the
dissolved metal that is assumed to be oxidized. (This
appears contrary to observation in many cases, however;
see Fig. 1 and associated text.)

Two objections raised to these mechanisms were 1)
that the blade metal itself should reduce Na_2SO_4 at 900 °C,
and 2) that the ability of NaCl to promote Na_2SO_4 hot
corrosion in the laboratory, a fact by then well
established, was not explained. Both effects (or lack
thereof) pointed to involvement of a protective oxide on
the metal which could shield the alloy from molten sulfate
attack until penetrated by the action of chloride or
reductant.

Since the era of Simon et al, few papers of
mechanistic significance have been concerned simply with

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'Na$_2$SO$_4$' corrosion; emphasis has almost invariably been on the subcategories listed in Table 1. One exception, to be discussed later, is a recent paper by Fryburg and coauthors (25) which examines Na$_2$SO$_4$ hot corrosion in detail.

SULFIDATION-OXIDATION

Many later researchers investigated sulfidation as the critical element in hot corrosion. Seybolt and Beltran (26) confirmed that nickel reacted with Na$_2$SO$_4$ to produce nickel sulfide. With Ni-20Cr, they observed chromium sulfide to form, but to then oxidize, releasing sulfur into the metal to produce new sulfide. For superalloys, enhanced oxidation of the Cr-depleted metal adjacent to the chromium sulfide phase appeared possible (27). Danek (28) summarized the principal theories existing in 1965 on the role of sulfidation in hot corrosion:

1. Cr$_2$S$_3$ forms, depleting the adjacent metal of chromium. The depleted metal then oxidizes rapidly and flakes off, carrying the sulfide with it.

2. Cr$_2$S$_3$ forms, with the sulfide then being oxidized, and in the process releasing S into the metal to form more Cr$_2$S$_3$.

3. The sulfide phase is actually Ni$_3$S$_2$ at temperature, but converts to Cr$_2$S$_3$ when the metal cools.

Whether sulfidation significantly increases the oxidation rate of blade metals was questioned for some time. The most recent work confirms that it does, if the sulfidation level is high enough. For example, Erdoes (29) showed that IN 713LC oxidizes rapidly at 900°C if sulfidized to 5-6 mg/cm^2 S, but not for lower S levels. The morphology was very similar to hot corrosion, with only some differences in the oxide structure parameters, which Erdoes attributed to the influence of sodium oxide.

Erdoes also identified the two predominant sulfides formed in the hot corrosion of IN 713LC as being not pure chromium sulfides, but rather 'Cr-Ti-S' (Cr$_3$S$_4$ containing Ti, Ni and traces of other alloy components but no Al) and 'Cr-Al-S' (a thiospinel containing Al, but no Ti). These sulfides have since been noted in the laboratory hot corrosion of Rene 80 (30).

The current view of sulfidation-oxidation is largely set forth by El-Dahshan, Whittle and Stringer (31). They

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differentiate between 'severe' and 'less severe' corrosion conditions. Under severe conditions (heavy deposits, high sulfur activity), an extensive network of large chromium-rich sulfides forms, predominantly following grain boundaries in the metal. The sulfides then oxidize, creating fingers of oxide that surround and isolate residual Ni- or Co-rich metal particles that become incorporated into the corrosion scale. The released sulfur penetrates into the alloy in advance of the oxidation front to produce new sulfides. Sulfidation-oxidation of this type can continue for extended periods without further introduction of sulfur.

Conversely, under less severe conditions, and principally with Al_2O_3-producing alloys, the initial Cr-rich sulfides form as small discrete particles within the metal. The adjacent alloy matrix is depleted of chromium, and subsequent oxidation appears to involve this Cr-depleted zone, which is now less capable of forming protective Al_2O_3 (recall that Cr in the alloy promotes Al_2O_3 surface oxide formation). The sulfide phases are again oxidized, but since they are discrete and possibly separated from the metal by an intervening oxide, the released sulfur tends not to penetrate into the metal but to be liberated as sulfur oxides. Continued corrosion, in this case, will thus require a replenishing source of sulfur.

A unique insight into sulfidation-oxidation can be gained from the study of 'cut-edge' hot corrosion. This refers to hot corrosion occurring when a preoxidized or coated metal is damaged or cut (as in preparing test specimens) so that the oxide (or coating)/metal interface is exposed to the corrosive salts and gases. It is most often seen in the laboratory, although sometimes identified in engines (32). Investigation of the cut-edge attack of CoCrAlY (22Cr, 11Al, 0.5Y) coated Rene 80 at 885°C showed that nickel sulfide was the critical species, and that the same morphology could be produced either by spray-coating with Na_2SO_4 or by diffusing NiS into the cut-edge region under argon at temperature and then admitting air (32). The corrosion morphology (Fig. 1) shows that i) large quantities of Ni are transported into the coating corrosion residue, forming metallic (verified by microprobe) Ni-Co particles, and ii) a massive 'CrS' phase is produced which oxidizes before the Ni-Co particles (although these also are later oxidized). Evidently liquid nickel sulfide diffuses into the CoCrAlY where Ni is displaced, as metallic Ni-Co, by chromium to produce chromium sulfide. Preferential oxidation of the 'CrS' then yields the characteristic 900°C corrosion morphology, i.e., metall.. Ni-r' particles embedded in a chromium oxide phase. ... cut-edge' attack provides a clear example where nickel sulfide can be seen to form first,

but then be transformed to chromium sulfide, as suggested earlier (33). The metallic particles occurring in the oxide in the corrosion of superalloys may therefore be partly metal taken into solution and then displaced from the sulfide phase and not simply 'bypassed' alloy fragments.

Another area of sulfidation-oxidation research recently pursued involves the reactions of metals or alloys with SO_2-O_2 mixtures; i.e., without any salt phase present. This work is concerned with the fundamental mechanisms of simultaneous sulfidation-oxidation (34), but also with hot corrosion, with many aspects of hot corrosion being surprisingly well reproduced (35,36).

Concern with sulfidation-oxidation also led Quets and Dresher (37), and Gulbranson and Jansson (38) independently, to develop 'phase predominance' diagrams to predict the metal, oxide, sulfide or other phase to be expected with M-O-S systems for given temperatures and sulfur and oxygen partial pressures. The method, derived from metallurgical thermodynamics, is based on the relation

$$\Delta G_T^O = -RT \ln K \qquad [7]$$

For reaction, e.g.,

$$2 M + SO_2 = M_2S + O_2 \qquad [8]$$

$$K = \frac{a_{M_2S} \, P_{O_2}}{(a_M)^2 \, P_{SO_2}} \qquad [9]$$

By setting the activities of the condensed phases at unity, the conditions for formation of M or M_2S can be defined simply in terms of T, O_2 partial pressure and SO_2 partial pressure. With proper selection of reactions and phase rule application, a phase diagram can be developed showing the regions of stability for all phases in the system in relation to O_2 and SO_2, or other gas species (S_2, SO_3 etc.) if desired (39). The results must be viewed with caution, since assumptions concerning equilibrium, activities, and other factors (e.g., 40) are invoked, but phase stability diagrams are valuable and widely used in hot corrosion research.

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BASIC-ACIDIC FLUXING

In the late 1960's-early 1970's, researchers began to consider Na_2SO_4 not simply as a source of sulfur, but as a basic fluxing medium capable of dissolving protective oxides from superalloy surfaces. Sodium sulfate dissociates according to

$$Na_2SO_4 = Na_2O \text{ (base)} + SO_3 \text{ (acid)} \qquad [10]$$
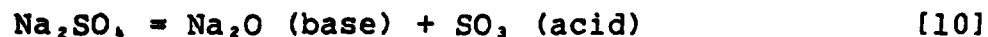
where, for 900 C, the equilibrium constant, K, is given by

$$K = a_{Na_2O} P_{SO_3} = \sim 10^{-16} \qquad [11]$$

Bornstein and DeCresente appear to have first proposed the basic fluxing mechanism, pointing out that Na_2SO_4 deposits become basic during corrosion (cf. reaction [2]), and showing that salts forming Na_2O but containing no sulfur ($NaNO_3$ and Na_2CO_3) gave accelerated oxidation similar to Na_2SO_4 (41). They subsequently investigated the reaction of molten Na_2SO_4 with various oxides, and demonstrated that hot corrosion was inhibited by oxides (e.g., Cr_2O_3) which reacted to reduce the melt Na_2O concentration, except for V_2O_5 and MoO_3 which they considered corrosive in themselves (42).

Goebel et al elaborated on the fluxing hot corrosion mechanism, and included acidic fluxing (43). Their theories are formulated on the basis of Fig. 2, which represents Al_2O_3 in equilibrium with Na_2SO_4 at 1000°C as a function of P_{SO_3} (or a_{Na_2O}) and P_{O_2}. According to Fig. 2, an Al_2O_3 scale should remain stable and protective in Na_2SO_4 under the oxygen and SO_3 partial pressures occurring in gas turbines; however, Goebel et al postulate that P_{O_2} is reduced at the salt-metal interface (as depicted by the arrow path in Fig. 2) by further oxide formation or other reactions to the point where sulfides can develop (by diffusion of sulfur through the oxide scale) in the underlying metal. The dashed lines in Fig. 2 are sulfur isobars showing that P_{S_2} sufficient for metal sulfide formation is readily attained in oxygen depleted Na_2SO_4. The combined oxygen and sulfur removal produces Na_2O levels which dissolve the protective Al_2O_3 scale by the basic fluxing reaction indicated, and accelerated oxidation commences.

Acidic fluxing, which the authors describe as catastrophic and self-perpetuating in contrast to basic fluxing which they consider as less severe and requiring continued deposition of Na_2SO_4, was found in Na_2SO_4 corrosion of alloys containing Mo, W or V. In this case, an acidic oxide, e.g., MoO_3, is thought to be formed by oxidation of Mo-rich particles in the alloy which

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increases the SO_3 concentration in the Na_2SO_4 phase by

$$Na_2SO_4 + MoO_3 = Na_2MoO_4 + SO_3 \qquad [12]$$

The acidified Na_2SO_4-Na_2MoO_4 melt then dissolves the protective Al_2O_3 by the acidic reaction shown in Fig. 2. Although MoO_3 may volatilize from the melt, the authors propose that it is continually replenished by oxidation of Mo in the alloy, and so the reaction tends to be self-sustaining.

The concept of hot corrosion via basic-acidic fluxing has received strong support from the quantitative measurements of the solubility of the different turbine metal oxides in Na_2SO_4 as a function of oxide (O^{2-}) activity by Rapp and coworkers (44) and Stern and Deanhardt (45). The results, gathered by Stern (46) in Fig. 3, show that the metal oxide solubility is drastically affected by the Na_2O concentration in Na_2SO_4, e.g., increasing to 10,000 ppm or higher for Na_2O levels below 10^{-13}.

CURRENT VIEW OF Na_2SO_4 INDUCED HOT CORROSION

Although basic fluxing reasonably explains initiation of hot corrosion, the role of fluxing in the propagation of hot corrosion has been unclear. However, recent research by Fryburg et al (25) elegantly details the reactions that may be involved in initiation and propagation of 900°C hot corrosion. The original paper should be consulted, but the main conclusions can be summarized from Figs. 4 and 5. By careful analysis of weight gain, SO_2 evolution, and water soluble species formed (a,b,c, of Fig. 4), the authors identified characteristic behaviors occurring in the 900°C corrosion of preoxidized B-1900 superalloy coated with Na_2SO_4. These data, coupled with thermodynamic analysis and metallurgical examination of specimens corroded for the various times, allowed Fryburg et al to postulate the reactions controlling the four stages of hot corrosion indicated in Fig. 5.

Without going into specific argument, the reaction scheme in Fig. 5 may be outlined as follows. A protective Al_2O_3 film forms on B-1900 during oxidation; however areas of the film may be rich in Cr_2O_3 or MoO_3 (from oxidized surface carbides). During the induction period, Cr_2O_3 and MoO_3 react with the deposited Na_2SO_4, producing soluble Na_2CrO_4 and Na_2MoO_4 and releasing SO_3 (partially detected as SO_2). Ultimately the Al_2O_3 film is 'breached' at local sites (the end of the induction period) and the sulfate film reacts with nickel in the exposed metal, rapidly consuming the sulfate and generating extensive NiS in the alloy. This reaction, however, also greatly increases the

O^{2-} concentration in the remaining Na_2SO_4, and the Al_2O_3 film, which until now has still been largely protective, is destroyed by basic fluxing as depicted in Fig. 5.

Once Al_2O_3 protectiveness is lost, the metal oxidizes rapidly, with MoO_3 being produced which reacts with oxide ion and other dissolved species in the sulfate melt to form Na_2MoO_4 (intermediate region in Fig. 5). Continued attack then leads to oxidation of the NiS (producing the SO_2 'blip' in Fig. 4b), and to the formation of a liquid Na_2MoO_4/MoO_3 acidic fluxing phase at the metal interface which prevents reformation of protective Cr_2O_3 or Al_2O_3 layers. At this point, oxidation becomes catastrophic. Corrosion may, however, be reduced or halted when only limited amounts of Na_2SO_4 are initially present, where the authors consider that solid $NiMoO_4$ rather than liquid MoO_3 would be formed, or by the substitution of Mo by, e.g., Ta which produces a solid ($NaTaO_3$) rather than liquid phase upon reaction with Na_2SO_4.

The work of Fryburg et al represents a 'state-of-the-art' explanation of the mechanism of Na_2SO_4 induced hot corrosion. It provides perhaps the best basis currently available for formulating new research or guiding turbine alloy development.

LOW TEMPERATURE HOT CORROSION

Although hot corrosion in the 700°C range had in fact been observed (47) and to a considerable extent explained (48), it was widely believed up to the mid-1970's that Na_2SO_4 was the essential cause of hot corrosion, and that there would be little attack below the Na_2SO_4 melting point (884°C). The British Navy had found maximum corrosion at 750°C in its shipboard gas turbines, with the formation of low melting complex alkali compounds being speculated as one of the possible causes (49), but even as late as 1977, hot corrosion was predicted to occur only above a threshold temperature of the order of 750°C (7). Experience in the development of US Navy marine gas turbines demonstrated that severe corrosion could occur ca. 700°C, and research was sponsored by the Navy in industrial (and Navy) laboratories to confirm the cause of this 'new' type of hot corrosion.

As a result of research initiated under the Navy program, there is now a broad-based understanding of 'low temperature hot corrosion' (LTHC), e.g., as given by Luthra and Shores (50). The open literature publications of several other researchers who have investigated LTHC are contained in the Proceedings of the 1981 International Conference on High-Temperature Corrosion (51). LTHC is generally agreed to result from formation of low melting

$CoSO_4$-Na_2SO_4 mixtures (eutectic mp 545°C) by the reaction of cobalt oxide and sodium sulfate deposits on the blade surface with SO_3 from the engine gas.

$$Co_3O_4 + 3\ SO_3 = 3\ CoSO_4 + 1/2\ O_2 \qquad [13]$$

$$CoSO_4 + Na_2SO_4 = CoSO_4\text{-}Na_2SO_4\ \text{(low melting} \qquad [14]$$
$$\text{mixed sulfate)}$$

Contrary to Na_2SO_4 hot corrosion, the SO_3 partial pressure is critical in LTHC with approximately 1×10^{-4} atm SO_3 required at 700°C for a molten phase to be formed and corrosion to occur (50). Corrosive $NiSO_4$-Na_2SO_4 molten mixtures may also be formed, but an ~5X higher SO_3 partial pressure is required (50,52). Nickel-base alloys containing no cobalt may thus be more LTHC resistant than cobalt-base metals. Resistance to LTHC generally improves with increasing Cr content of the alloy or coating.

Low temperature hot corrosion normally produces (and is identified in engines by) a characteristic pitting attack where cobalt (or nickel) is transported from the pit into the outer corrosion layer, and there is little sulfide formation or depletion of Cr or Al in the metal in advance of the corrosion front. However, this morphology has been reported to change to the sulfide-producing '900°C morphology' for thick deposits (48) or long times (600 hrs for Nimonic 105 superalloy) at 750°C (21). In each case, limited access of oxygen through the thick corrosion scale is suggested to cause the transition to sulfidation corrosion. Further investigation of the possible change between sulfation and sulfidation modes of attack is warranted, since this relates importantly to identification of corrosion in gas turbines, and the ultimate understanding of the corrosion process.

Current LTHC research is concerned, e.g., with the thermodynamics of molten sulfate mixtures (53), the effects of other elements (e.g., Mn, Zn) which can also produce low melting mixed sulfates on the blade surfaces (54,55), and quantitative understanding of the reactions and transport mechanisms of low temperature hot corrosion (56).

HOT CORROSION EFFECTS OF NaCl

Because of the high NaCl content of sea salt, NaCl effects in hot corrosion have long been of concern with marine gas turbines. The results of many British studies are documented, e.g., in the review by Condé and McCreath (9). Similarly, the US Navy sponsored considerable study to determine whether NaCl had significant effects in LTHC. Most of this research was not published in the open

literature, but it dealt with, among other things, the 650-700°C corrosion of CoCrAlY and aluminide coatings deposited with NaCl or Na_2SO_4 and exposed to SO_3-air, the conversion of NaCl to Na_2SO_4 by SO_3 on different metal and metal oxide surfaces, and assessment of mechanical or chemical damage that might result from NaCl particle impaction on blade surfaces. Substantial research has also been supported by NASA on the role of NaCl in gas turbine hot corrosion, as summarized by Kohl, Stearns and Fryburg (57).

Essentially two questions are involved: i) whether NaCl is converted to Na_2SO_4 during combustion so the blades actually see only Na_2SO_4, and ii) whether NaCl is uniquely corrosive if condensed or vaporous NaCl does contact the blade surface. With regard to i), NASA burner rig experiments showed that injected NaCl or sea salt was completely converted to sulfate in the 2.2 millisecond residence time of the salt in the burner (58). This contradicts an earlier study (59) which indicated that more than 8 ms was required for Na_2SO_4 formation, with some NaCl therefore likely to survive the 5-7 ms gas turbine combustor residence time. The controversy was rendered moot, however, by the subsequent showing that NaCl particles shed from the compressor blades could reach the 1st stage turbine blades without being sulfated (60).

Presumably the blade surface is exposed to NaCl therefore, and question ii) is evoked as to whether this significantly accelerates hot corrosion. The evidence divides into 'pro' and 'con' statements. The addition of NaCl in bulk Na_2SO_4 (crucible) tests is well known to increase hot corrosion. It has also been well demonstrated that vapor phase NaCl can disrupt surface oxides (61), even at ppm levels (62). In addition, several published (e.g., 30) and unpublished studies indicate that NaCl vapor affects the corrosion of Na_2SO_4 deposited metals.

On the other hand, thin films of NaCl are very quickly converted to Na_2SO_4 at the SO_3 partial pressures encountered in gas turbines. Also, NaCl has been shown to produce a characteristic attack, especially with CoCrAlY where the CoAl phase is preferentially attacked with extensive porosity and internal oxidation resulting (63), which has not been found on corroded CoCrAlY coated gas turbine blades. In Navy sponsored LTHC studies with thick (5 mg/cm^2) predeposited NaCl on CoCrAlY, two sequential reactions were seen to occur: the SO_3 first sulfated the NaCl, and then reacted with the resultant sulfate and CoCrAlY to produce molten $CoSO_4$-Na_2SO_4 and L. T. hot corrosion (64). Characteristic NaCl corrosion occurred in the several hrs required for NaCl sulfation, but then the morphology changed to that typical of LTHC with no

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apparent effect of the 'precorrosion'. For the very low NaCl concentrations expected on turbine blade surfaces, it is thus unlikely that the NaCl sulfation step would have any significant effect. If NaCl particles are driven into the salt/oxide layer on the blade so as to be shielded from SO_2, the corrosion process could be affected; convincing evidence to this point has been presented for helicopter gas turbines (65). However, studies in the US Navy program using 10 μm NaCl particles at ~100 meters/second failed to show accelerated corrosion as a result of impaction (66).

Thus NaCl is clearly corrosive at high temperatures, but because of its strong reaction with SO_2, it appears to act principally as a source of Na_2SO_4 in most gas turbine circumstances. Disruption of protective oxides by traces of NaCl may enhance hot corrosion, however, and in other combustion systems, e.g., burning of coal with high chlorine and low sulfur content, 'chloride attack' could be a dominant mode of corrosion.

CONCLUSION

Written for the nonspecialist in hot corrosion, this review has been intended to delineate the development of the different hot corrosion theories, and to provide a brief sketch of the central ideas of each, along with the relevant literature references. It has also been meant to convey the author's view that the various theories are not basically in conflict, but only logical extensions of different approaches to the study of hot corrosion.

ACKNOWLEDGMENTS

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'CUT-EDGE' HOT CORROSION
OF BC-21 COMPOSITION
CoCrAlY INDUCED BY NiS
AT 885°C.
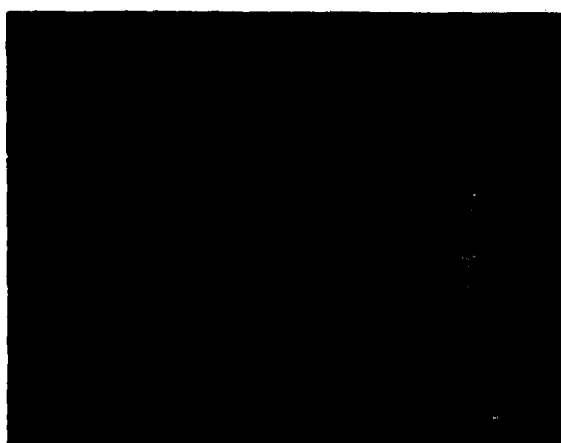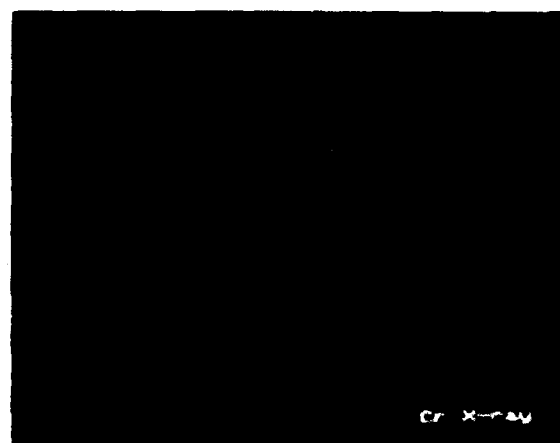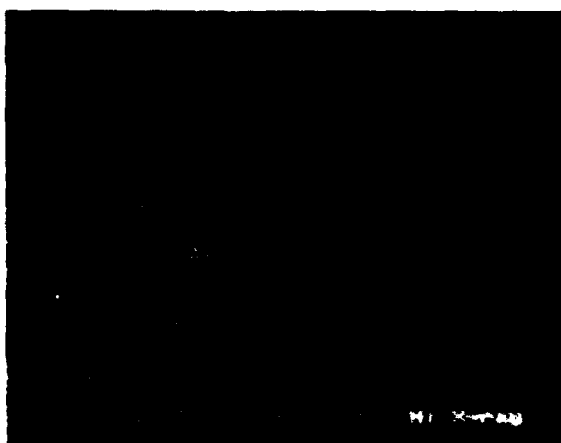
Fig. 1   'Cut-Edge' hot corrosion of BC-21 CoCrAlY coated
          Rene 80 induced by NiS interdiffusion at 885°C.
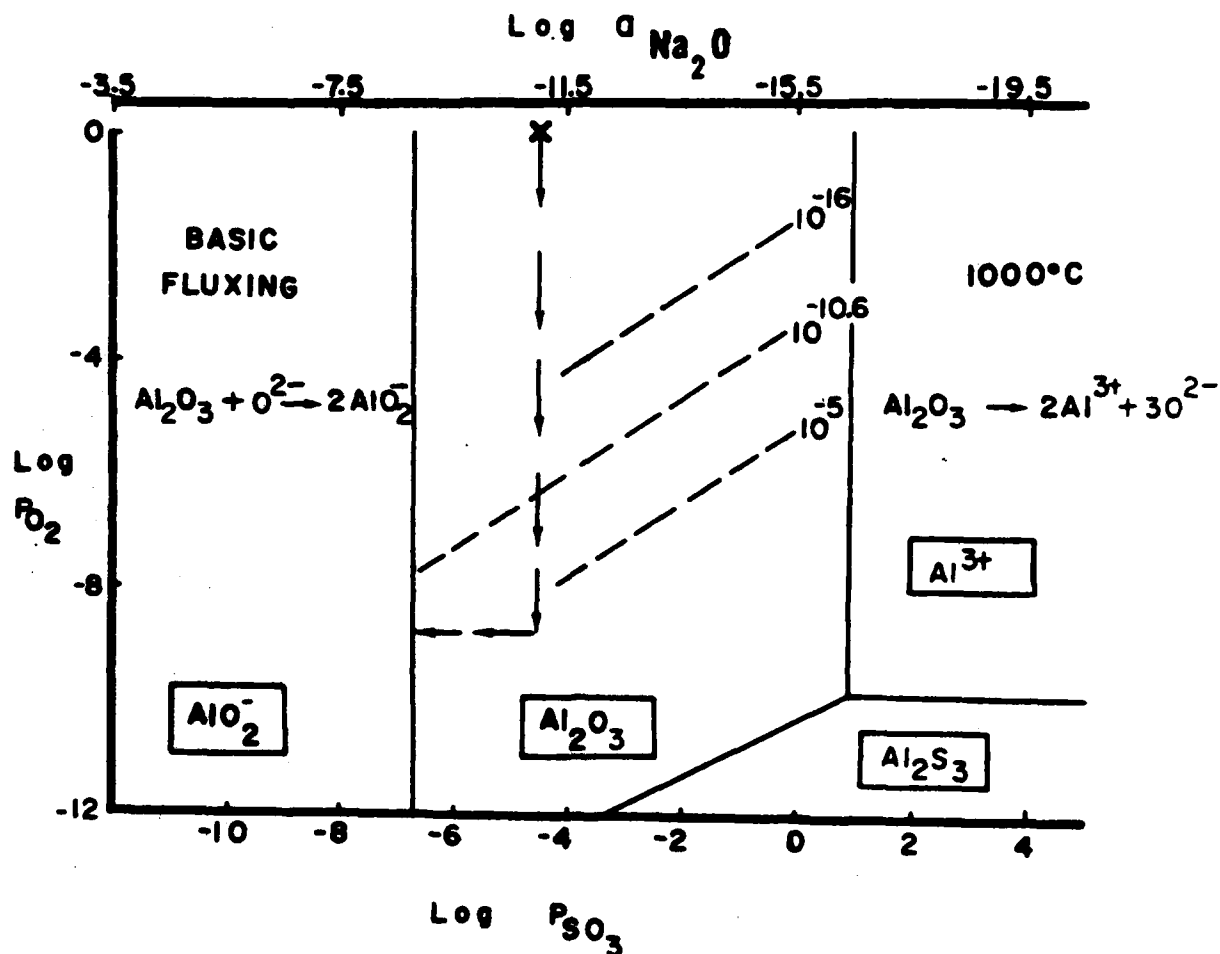
Log a_{Na_2O}

-3.5   -7.5   -11.5   -15.5   -19.5

BASIC
FLUXING

10^{-16}

1000°C

$10^{-10.6}$

$Al_2O_3 + O^{2-} \longrightarrow 2AlO_2^-$

10^{-5}

$Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$

Log P_{O_2}

Al^{3+}

AlO_2^-

Al_2O_3

Al_2S_3

-10   -8   -6   -4   -2   0   2   4

Log P_{SO_3}

Fig. 2   Stability diagram indicating change in Na_2SO_4 basicity (Na_2O activity) during hot corrosion (from F. S. Pettit, MCIC-75-27; reproduced by permission of Metals and Ceramics Information Center).
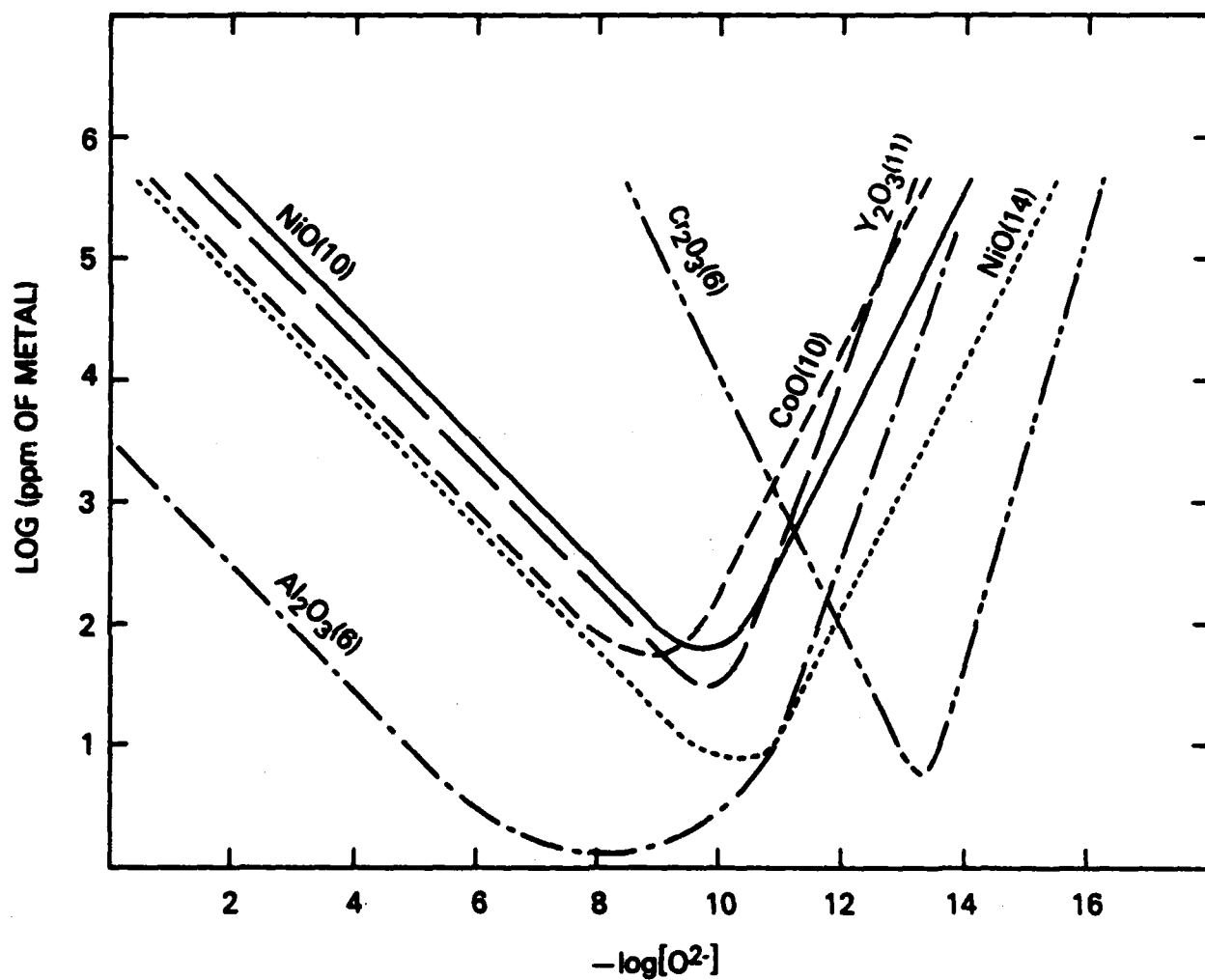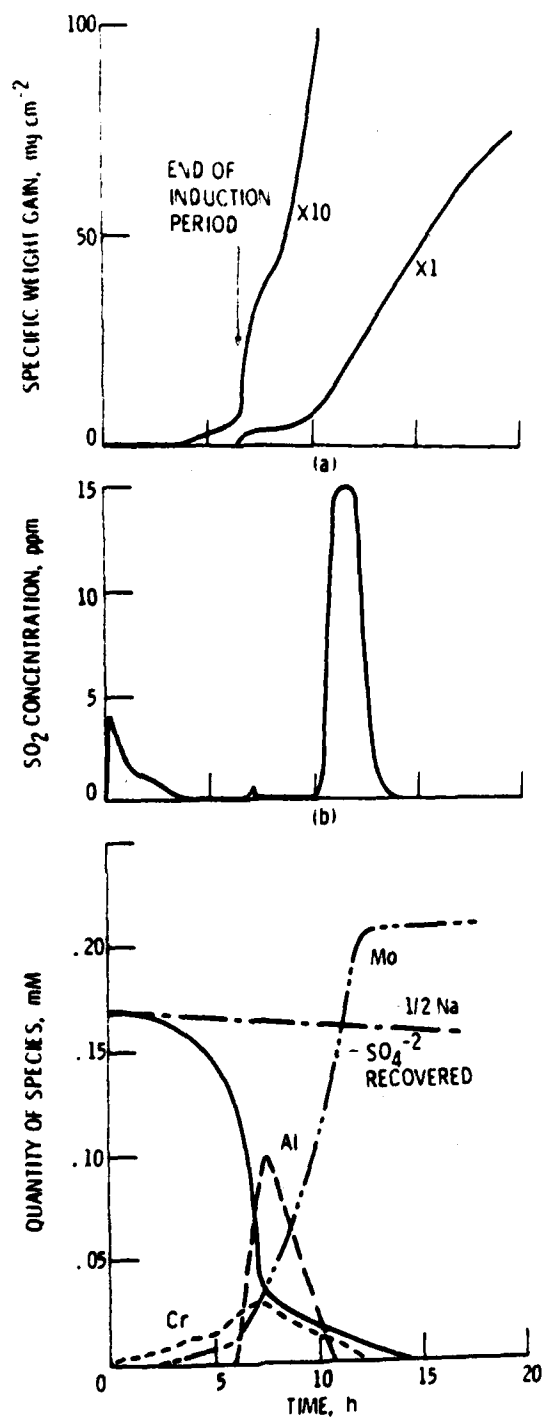
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Fig. 3 Solubility of oxides in Na$_2$SO$_4$ at 1200 K as a function of Na$_2$O activity (from K. H. Stern, Ref. 46).

Fig. 4 Hot corrosion of B-1900 coated with 3 mg/cm²
Na₂SO₄ at 900°C, indicating weight gain (a), SO₂
evolution (b), and water soluble species in salt
(c) (from G. C. Fryburg et al, J. Electrochem.
Soc. **129**, 571 (1982); reproduced by permission of
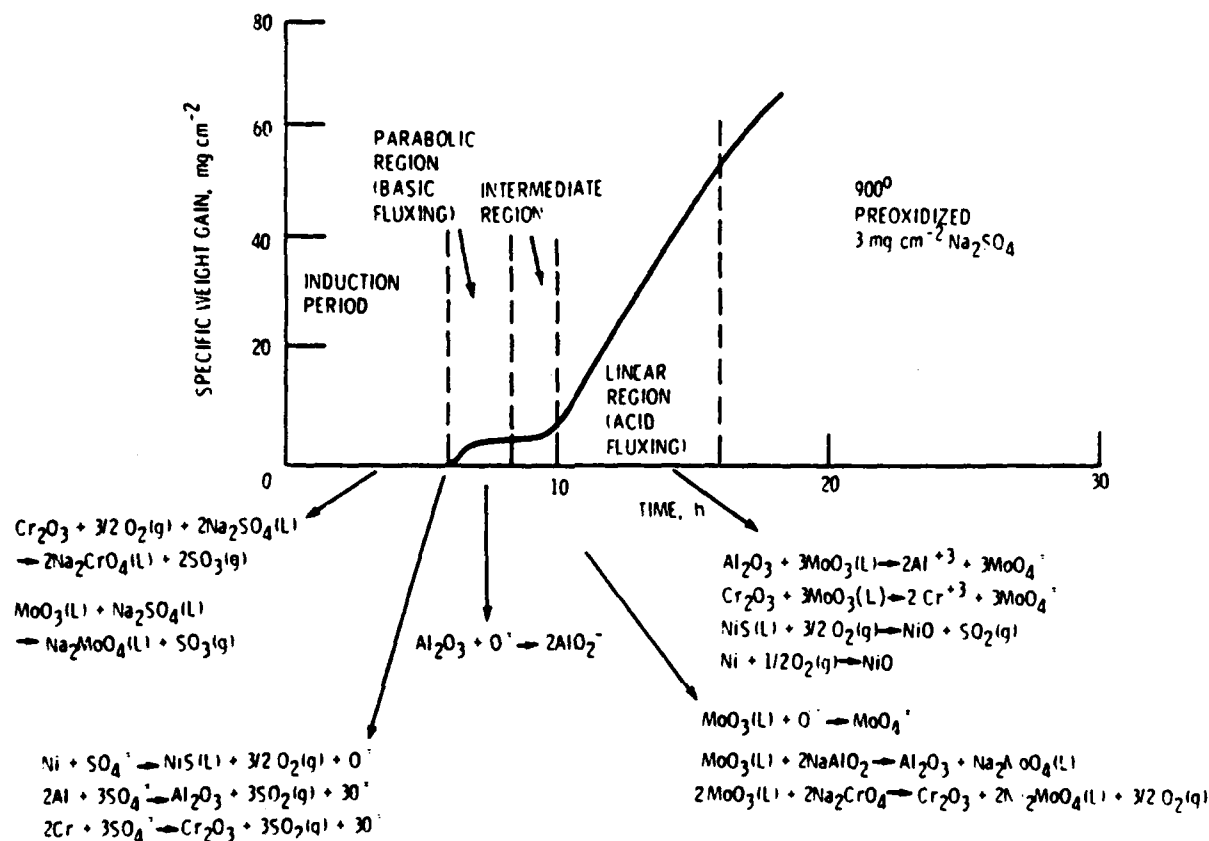The Electrochemical Society).

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Fig. 5   Summary of chemical mechanism of hot corrosion
(from G. C. Fryburg et al, J. Electrochem. Soc.
129, 571 (1982); reproduced by permission of The
Electrochemical Society).

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